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PHOTOGRAPHIC IMAGE ENHANCEMENT USING CHEMILUMINESCENT AND FLUORESCENT LIGHT

C. Leung, R. G. Manning, R. R. Pettijohn, and Z. Reyes
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Contributions by: M. Scolnick, SRI International
M. Thackray, Australian Atomic Energy Commission

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The goal of this research program was to develop methods analogous to auto-radiographic photographic image enhancement in which light instead of nuclear radiation is emitted from the photographic image. These methods would allow images to be intensified without the inconvenience and limitations that result from the currently required radionuclides.

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20 ABSTRACT (Continued)

Fluorescence and chemiluminescence methods suitable for photographic image enhancement have been investigated, and the feasibility of both approaches has been demonstrated. Fluorescent images were obtained by chemically reacting uv-fluorescent dyes with silver bromide or silver iodide bleached images. Fluorescence quenching after reaction has been solved by transfer of the dye image to pretreated plastic. Chemiluminescent images were obtained by copper(II) catalyzed oxidation of luminol at or near the site of the original image silver grain. The original negative was either toned to copper sulfide or physically developed to deposit a thin layer of metallic copper on the image silver grains.

The chemiluminescent or fluorescent light emitted from the images is proportional to the optical density of the silver in the original negative-- even at extremely low densities. Exposure of a light-sensitive film using a lens focusing system results in a new image in which the degree of intensification is controlled by the exposure duration.

In contrast to the autoradiographic technique, which is limited in resolution by the range of the radiation, the resolution transfer capability of the fluorescence and chemiluminescence intensification technique is limited in theory primarily by the resolution of the original negative and the resolution capability of the photographic reimaging system. This significant attribute is a result of the ability to focus and thereby faithfully transfer the fluorescing or chemiluminescing image onto a photographic film.

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SUMMARY

The goal of this research program was to develop methods analogous to autoradiographic photographic image enhancement in which light instead of nuclear radiation is emitted from the photographic image. These methods would allow images to be intensified without the inconvenience and limitations that result from the currently required radionuclides.

Chemiluminescence and fluorescence methods suitable for photographic image enhancement have been investigated, and the feasibility of both approaches has been demonstrated.

The chemiluminescent or fluorescent light emitted from the images is proportional to the optical density of the silver in the original negative—even at extremely low densities. Exposure of a light-sensitive film using a lens focusing system results in a new image in which the degree of intensification is controlled by the exposure duration.

In contrast to the autoradiographic technique, which is limited in resolution by the range of the radiation, the resolution transfer capability of the fluorescence and chemiluminescence intensification technique is limited in theory primarily by the resolution of the original negative and the resolution capability of the photographic reimaging system. This significant attribute is a result of the ability to focus and thereby faithfully transfer the fluorescing or chemiluminescing image onto a photographic film.

The highest quality fluorescing images obtained to date have been achieved by use of a fluorescent dye image transfer technique. The fluorescent dye is first absorbed onto an original negative that has been bleached to silver bromide or silver iodide. The fluorescent dye image is then transferred under laminar pressure to a receiving medium, composed of a gelatin layer on thin plastic, that is soaked with a wetting agent and/or mordant. The wetting solution acts as a solvent for the dye on the image and allows rapid diffusion of the dye into the receiving gelatin. The mordant insolubilizes the dye on the receiving substrate and prevents diffusion with resulting loss of image resolution. Images toned with acriflavine and rhodamine B and transferred to a receiving medium were intensely fluorescent under uv illumination.

Photographs of these fluorescent images have been made using a variety of broad-band filters and film types to improve the signal-to-noise ratio. Typical exposure times ranged from 30 sec to 10 min. The resolution of the intensified imagery obtained by this method is on the order of 25 lp/mm. We believe the resolution is severely limited by the present camera optics and close-up focusing capabilities. Sensitometric evaluation of the intensified imagery has indicated a definite increase (twofold) in effective speed compared to the original imagery.

The most favorable chemical system found to date for obtaining chemiluminescent photographic images is the copper-catalyzed oxidation of luminol. Two approaches have given promising results. One approach entails the deposition of copper on the original negative using ferrous-ferric redox physical development. The copper plates out on the silver grains, forming a thin metallic coating on the original image. The second procedure requires the formation of copper sulfide on or at the site of the original image silver grain.

We have constructed an apparatus consisting of a 300-cc plate glass tank that is filled with a dilute basic luminol solution containing hydrogen peroxide and postassium carbonate. The background luminosity of this solution is efficiently controlled by recirculating the solution through a trap containing Chelex-100 resin.

A photograph toned with metallic copper or copper sulfide is then mounted and placed in the glass tank with a high rate of recirculation. The chemiluminescence is visible to the eye and can be photographed with exposure times ranging from 1 to 30 min depending on the solution characteristics. Photographs having resolutions of 10 lp/mm have been made, and resolutions should increase dramatically as procedures are improved. Intensification of photographic imagery has not yet been demonstrated using the chemiluminescence technique, but the feasibility of the procedure has been shown.

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ILLUSTRATIONS

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I   INTRODUCTION

Under a one-year contract to the Office of Naval Research (ONR),
SRI International was begun to develop chemiluminescence and fluorescence
methods suitable for photographic image enhancement. The goal of this
research program was to develop methods analogous to autoradiography in
which light instead of nuclear radiation is emitted from the photographic
image. The methods would allow images to be intensified without the
inconvenience and limitations that result from the currently required
radionuclides. The techniques were to be applicable to both under-
exposed imagery and low-density regions of properly exposed imagery.
The methods make use of the metallic silver present in developed original
negatives, so that the light emitted from the chemiluminescing or
fluorescing image will be proportional to the optical density of silver
in the original negative, even at extremely low densities. The chemi-
luminescing and fluorescing image can then be photographed, with the
duration of exposure controlling the degree of intensification achieved
in the resulting image.

This final report of the year's research includes a background
discussion describing the radiotoning approach, a general technical
discussion of the chemiluminescence and fluorescence methods we are
using to enhance photographic images, and separate chapters describing
research on fluorescence, delayed fluorescence, and chemiluminescence.
The summary section includes a statement of progress and suggestions
for continued research that should improve these two promising methods
of photographic intensification.

II BACKGROUND

Eugene Ostroff of the Smithsonian Institute was the first to use radioactive isotopes to enhance faded photographs.[1-2] To counteract the fading, caused by oxidation of the silver in his old photographs, he neutron-irradiated these photographs and converted the silver to the radioactive isotope silver-108. The intensification was then made by contacting the radioactive image to a piece of unexposed x-ray film. An enhanced image (autoradiograph) was obtained that could be controlled by varying the time in which the radiation was allowed to expose grains on the new photographic film. A severe limitation to this neutron activation technique was that impurities other than silver were also activated during the neutron irradiation. The chlorine and sodium in the gelatin were highly activated, and their radiations tended to fog the autoradiograph. Another drawback was that silver-110m is also activated and emits a very energetic gamma particle, and the long range of this gamma caused the imagery obtained to be of very low resolution.

To avoid these limitations, Malcolm Thackray of the Australian Atomic Energy Commission (AAEC) developed a method that uses isotopically pure radioactive solutions.[3,4] The underexposed silver image was rendered radioactive through chemical techniques. Thackray's early work with beta-particle-emitting S-35 demonstrated the feasibility of the radiotoning approach, and the potential of this technology attracted the attention of the United States intelligence communities.

Under sponsorship of the U.S. Navy, SRI International has achieved a state-of-the art capability in the field of nondestructive methods of intensifying the image of original negatives by the use of radioisotopes

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With these procedures, we have successfully demonstrated increased optical density, contrast, effective film speed, and resolution of photographic imagery, and thereby increased the information derivable from original negatives.

Unfortunately, the application of the radioisotope technique is limited because it requires specialized equipment and personnel trained in radiochemistry.

The remainder of this report describes SRI's development of methods analogous to autoradiography, by which images can be intensified without the limitations imposed by use of radionuclides.
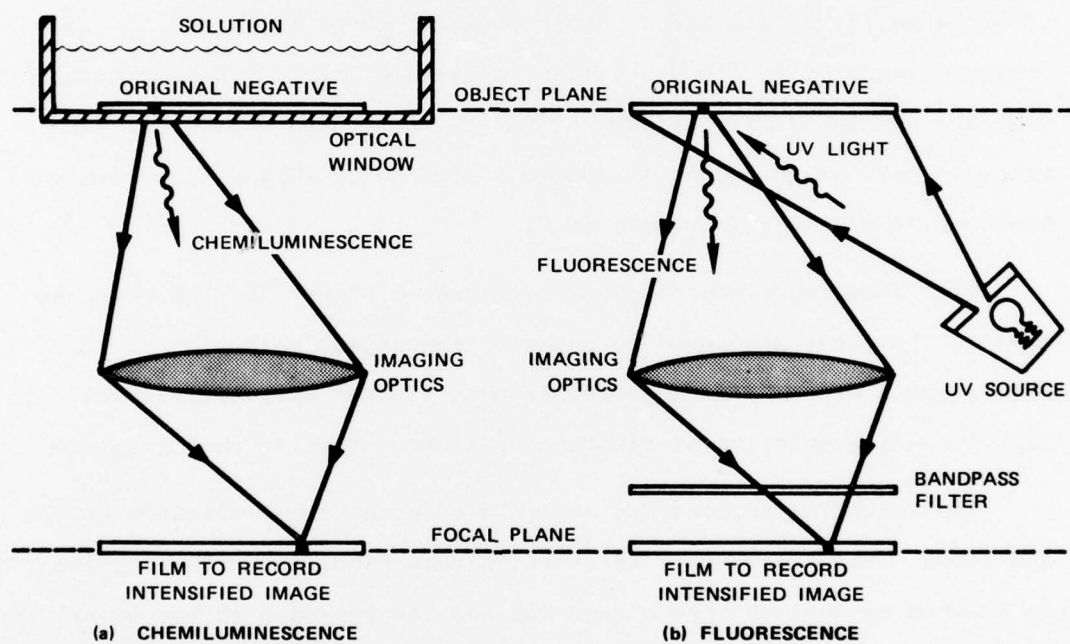
III THE FLUORESCENCE AND CHEMILUMINESCENCE
INTENSIFICATION TECHNIQUES

Figure 1 illustrates, in a conceptual way, how the emitted light from an original negative can be collected and focused onto another film. With the chemiluminescence technique, shown in Figure 1a, the original negative is flooded with a solution of chemiluminescent molecules that are catalytically oxidized at the silver grains. The reaction products emit light, and the reactions proceed as long as the chemi-luminescent solution is replenished.

With the fluorescent technique, shown in Figure 1b, the original negative is first processed to deposit fluorescent molecules at the silver grain sites. The negative is then flooded with ultraviolet light, causing emission of fluorescent light, which is photographed.

The reimaging process can be achieved with high resolution optics and films. The increase in information content of the resulting image is limited by the nonimage silver fog and the presence of low or extremely low optical density image silver in the original image as well as the signal-to-noise ratio achievable with the optimized intensification technique.

The resolution capability of the nuclear intensification technique is limited by the resolution of the original negative, the resolution of the autoradiographic film, the evenness of autoradiographic film contact during exposure, and the range of the radioactive emissions. Since the random direction emissions cannot be conveniently focused, the highest resolution intensification is obtained by contact autoradiography. Each radiotoned silver grain in the original negative induces

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SOLUTION

ORIGINAL NEGATIVE   OBJECT PLANE   ORIGINAL NEGATIVE

OPTICAL
WINDOW   UV LIGHT

CHEMILUMINESCENCE   FLUORESCENCE

IMAGING   IMAGING
OPTICS   OPTICS   UV SOURCE

BANDPASS
FILTER

FOCAL PLANE

FILM TO RECORD   FILM TO RECORD
INTENSIFIED IMAGE   INTENSIFIED IMAGE

(a) CHEMILUMINESCENCE   (b) FLUORESCENCE

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FIGURE 1   CONCEPTUAL ARRANGEMENTS FOR PRODUCING INTENSIFIED IMAGES WITH
CHEMILUMINESCENT OR FLUORESCENT LIGHT

Focal plane can contain photographic film or photocathode.

a diffuse spot on the autoradiograph caused by $1/r^2$ intensity gradient, where r is the range of the decay particle.

In contrast, the resolution transfer capability of the fluorescence and chemiluminescence intensification techniques is limited in theory primarily by the resolution of the original negative and the resolution capability of the photographic reimaging system. This significant attribute is a result of the ability to focus and thereby faithfully transfer the fluorescing or chemiluminescing image onto a photographic film.

The autoradiographic intensification method is primarily limited to the use of films that are sensitive to radioactive emissions, such as those containing x-ray and nuclear track emulsions. The reimaging film exposed to fluorescing or chemiluminescent light can be selected to optimize sensitivity in the emitted wavelength region and also to allow selection of the resulting intensified image's contrast or sensitometric gamma.

IV FLUORESCENCE

Fluorescent Dye Image

We first attempted to obtain a fluorescent photographic image using color development procedures. The silver image was bleached to AgBr, with a solution of 4% $K_3Fe(CN)_6$ and 2% KBr. The image was then developed with p-diethylamino aniline in the presence of a color former, which reacted with the oxidized developer to produce a dye image in situ with the silver image. Gray scale experiments were carried out with color formers 2,6-dichloro-5-hydroxy-1-naphthol, cyanoacetyl coumarone, acetoacetanilide, 5-amino-1-naphthol-acetonitrile, rhodanine, and 1-naphthol. Although some of these color formers are fluorescent, none of the dye images were fluorescent. Subsequent removal of the silver with bleach-fix solution, leaving the dye isolated in the gelatin matrix, also did not result in fluorescing images.

The first fluorescent images were obtained by bleaching the original negative to silver iodide followed by treatment with a fluorescent basic dye in acidic solution. The basic dyes tested were acridine orange, acriflavine, pyronin GS, rhodamine B, and safranine T. The dye was absorbed onto the silver iodide image, but the fluorescence of the dye was completely quenched on becoming absorbed. However, when the dye was complexed with phosphotungstic acid and the image silver iodide subsequently removed by fixation, fluorescent images were obtained. Unfortunately, the acridine orange and acriflavine image fluorescence decreased as a function of the duration of uv irradiation. After 1 hr, the fluorescence had decreased to about half the original level. The uv-induced degradation of fluorescence is most likely caused by oxidation

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of the dye and could possibly be controlled by nitrogen purging of the photographic system.

The rhodamine B image, however, does not appear to lose fluorescence during uv irradiation. The initial red color of the image eventually fades to an orange-pink color after a week, but the fluorescence is not diminished.

The primary disadvantage of this technique is that it destroys the original imagery. This procedure requires that the original silver first be converted to a dyed image and stabilized by formation of a phosphotungstic acid complex with the dye molecule. To obtain the fluorescing image, the original image silver must be irreversibly removed. Since the goal of this research program is to develop a non-destructive method of image enhancement, alternative methods were developed.

Evaluation of Fluorescamine as a Fluorescent Toner

Fluorescamine, 4-phenylspiro[furan-2(3H),1'-phthalan]-3,3'-dione, is a reagent for assaying primary amines. It reacts almost instantaneously at room temperature with primary amines to produce highly fluorescent compounds.

In preliminary tests with fluorescamine (FA), we acetylated the gelatin film to prevent reaction of FA with the amino groups in the photographic gelatin. The image was then bleached to silver bromide and toned with 6-amino-2-mercapto benzthiazole. The toned image was immersed in a solution of 5 mg FA in aqueous acetone at pH 8. The brilliant fluorescence of the FA reaction product was uniformly distributed over all the film. It is possible that acetylation of the gelatin was incomplete. We expected FA to react with the amino group of the 6-amino-2-mercapto benzthiazole.

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In another test, acriflavine was reacted with fluorescamine and the product was used as a toner. The image was bleached to silver iodide and was then treated with a solution of the FA-acriflavine reaction product. The fluorescence of the toned image was comparable to that obtained with plain acriflavine. No further work was done with FA.

Fluorescent Image Transfer

Four basic steps are required for fluorescent image transfer: (1) bleaching the original negative, (2) adsorption of the fluorescing dye on the bleached image, (3) chemical treatment of the receiving medium, and (4) transfer of the fluorescent dye.

The original negative image was first converted to silver iodide by treatment with an aqueous solution containing 4% $K_3Fe(CN)_6$ and 2% KI. The bleaching time varied from 0.5 to 6 min depending on the film type of the original negative. A number of water rinses to remove the bleach solution from the gelatin were followed by a 1-min treatment in 20% Na_2SO_4 solution (to harden the gelatin) and another rinse.

The images were toned by gentle agitation in the fluorescent dye solution. The composition of solutions tested and their corresponding adsorption durations are shown in Table 1.

Table 1

FLUORESCENT DYE ADSORPTION SOLUTIONS[*]

Fluorescent Dye	g%	Glacial Acetic Acid (ml%)	Toning Time (min)
Acridine orange	0.2	2	3
Acriflavine	0.5	2	3
Pyronin GS	0.2	2	3
Rhodamine B	0.2	0.5	0.5 - 4
	0.1	0.25	0.5 - 4
Safranine-T	0.3	0.75	10

[*] The solutions were brought to 100 ml with distilled water.

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After toning, the films were washed with water until the nonimage dye was removed from the film.

Preliminary dye transfer tests have been conducted using a gelatin coating on Mylar as the receiving substrate. This substrate was obtained by removing the image silver of a roll of Eastman Kodak Hi-Definition Aerial Safety film (Estar thin base) Type 1401 by fixation. The conditioning of this receiving medium consisted of soaking the film in wetting agent and/or mordant. The wetting solution acts as a solvent for the dye on the image and allows its rapid diffusion into the receiving gelatin. The purpose of the mordant is to insolubilize the dye on the receiving substrate.

A 1% aqueous solution of either Ethoquad C/12 [methylbis(2-hydroxyethyl) cocoammonium chloride, Armak Chemicals] was used as the wetting agent. Phosphotungstic acid (PTA) and naphthalenesulfonic acid (NSA) at concentrations of 1% to 5% in water were used as mordants. To evaluate the effect of the mordant and wetting agent treatments, the receiving sheets were conditioned by treatment with (1) first a mordant and then a wetting agent, (2) mixtures of mordant and wetting agent, (3) a mordant alone, and (4) a wetting agent alone.

The dyed original image was rinsed with water, and the excess liquid was removed with a rubber squeegee. Then the dyed image and the pretreated receiving substrate were pressed together in a laminator (Laminex 18-25) at room temperature. The films were guided through the laminator rubber rolls between sheets of Mylar. Contact of the image and receiving sheet was maintained for 5 min in a vacuum frame. The two films were then peeled apart, the transferred image was briefly rinsed with cold water, and the film was dried. The original toned image was rinsed, and either it was retoned for additional image transfers or the dye was removed and the silver image was restored.

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It was found that PTA and Ethoquad C/12 react to form a water-insoluble salt that streaks the transferred image; this combination was therefore unsuitable. Dye transfer was achieved with sheets conditioned with NSA-Ethoquad C/12, NSA-Tween 20, PTA-Tween 20, Tween 20, and Ethoquad C/12. Although all the transferred images fluoresced under uv light irradiation, the sharpest images showing the most intense fluorescence were obtained on receiving sheets conditioned with the 1% Ethoquad C/12 solution for 3 min before transfer. Images toned with acriflavine and rhodamine B yielded transfer images of comparable quality and were significantly sharper than those obtained with the other three dyes tested.

Fluorescent Image Photography

The toned film was irradiated with ultraviolet light from either an argon ion laser or a commercial lamp. The three optical configurations utilized are shown in Figure 2. The laser, a Coherent Radiation Model 52G-A, was tuned to a dual line output at 351.1 and 363.8 nm. The collimated beam was expanded through a 12-μm pinhole and had a flux of 4×10^{-5} watt cm^{-2} at the toned film surface. Since the laser output included a plasma halo of visible light, a Corning bandpass filter (300-400 nm bandpass, C.S. No. 7-60) was placed in front of the beam expander when optical configuration II was used (see Figure 2).

The uv lamp was an Ultra-Violet Products Inc. Model UVSL-25, which could be operated in two broadband (long wave and short wave) modes. Both configurations were used in conjunction with the 300-400 nm filter. The flux in either mode was measured to be about 3×10^{-5} watt cm^{-2} at the image using a United Detector Technology Model 21A power meter.

The fluorescing image was photographed using a Graflex Inc. Crown Graphic Model bellows camera equipped with an f 4.7, 135-mm Xenar lens. The film used was either Polaroid Type 55 Positive/Negative 4 x 5 inch
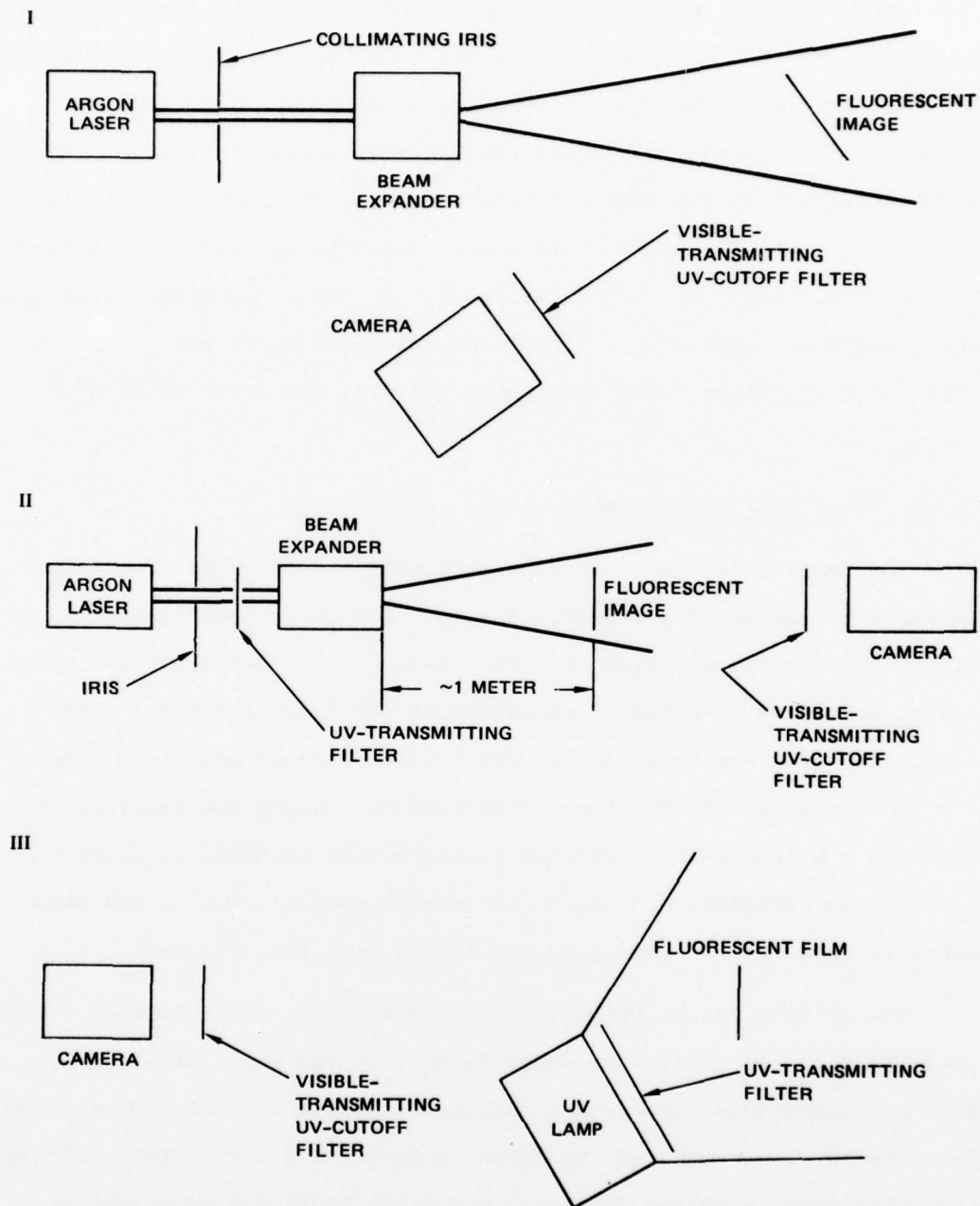
FIGURE 2   SCHEMATIC OF OPTICAL TRAIN

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film (50 ASA, resolution of 22-25 lines mm^{-1} positive or 150-160 lines mm^{-1} negative) or Kodak Royal Pan Film Type 4141 (400 ASA, resolution of 80 lines mm^{-1} negative). Because reflected uv light could expose these films, a Kodak Wratten sharp cut filter, C.S. No. 3 (435-nm uv cutoff), was placed in front of the camera lens. Exposure times, which were varied depending on the density of the original negative and the amount of fluorescent dye transferred, ranged from 10 to 45 min.

Table 2 shows a comparison of gray scale densities between an original negative (Kodak Type 1414 aerial film) and negatives obtained by exposure to its fluorescent light emission. In all three cases the transfer dye was rhodamine B. Assuming that a minimum acceptable density above base fog of 0.3 optical density units is the threshold for information retrieval, all three exposed and developed images exhibit at least two gray scale (one f-stop) steps of enhancement corresponding to a doubling of the effective photographic speed. Polaroid Type 55 film was used to obtain the Table 2 results. Under our conditions of low contrast, it exhibited better signal-to-noise ratios than the short wave mode in exciting the rhodamine B.

A comparison of laser and lamp light sources is shown in Figure 3. The original negative was properly exposed and was toned with rhodamine B. Parts b and c show that the coherence of the laser results in moire ring patterns superimposed on the original image. This problem, along with the greater expense involved in using a laser, indicates that a filtered uv lamp may be the preferable light source.

Studies with Itek tri-bar resolution targets indicate that our current resolution capability is 25 lines mm^{-1}, which is much less than the capacities of the two photographic films used. We are limited by the optics of the Crown Graphic bellows camera, the coarseness of the focusing mechanism, and the image-to-fog fluorescence ratio.

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Table 2

COMPARISON OF THE OPTICAL DENSITOMETRY OF AN ORIGINAL NEGATIVE
GRAY SCALE AND ITS CORRESPONDING FLUORESCENT-IMAGE EXPOSED NEGATIVES

(Optical Density Units)

| Step No.	Original Negative	Original- Base Fog	A1* (D-105, Long Wave)	A1-* Base Fog	A2† (D-105, Short Wave)	A2-† Base Fog	A3† (D-67, Short Wave)	A3-† Base Fog
1	1.34	1.07	1.16	0.50	1.22	0.69	1.12	0.60
2	1.23	0.86	1.14	0.48	1.19	0.66	1.08	0.57
3	1.08	0.81	1.12	0.46	1.18	0.65	1.00	0.48
4	0.86	0.59	1.10	0.44	1.18	0.65	0.85	0.43
5	0.65	0.38	1.09	0.43	1.16	0.63	0.92	0.40
6	0.48	0.21	0.97	0.31	0.98	0.45	0.84	0.32
7	0.38	0.11	0.97	0.31	0.95	0.42	0.82	0.30
8	0.32	0.05	0.91	0.25	0.87	0.35	0.78	0.26
9	0.28	0.02	0.80	0.14	0.72	0.19	0.68	0.16
10	0.28	0.01	0.81	0.15	0.70	0.17	0.61	0.09
11	0.27	0.00	0.76	0.10	0.64	0.11	0.55	0.03
12	0.27	0.00	0.66	0.00	0.53	0.00	0.52	0.00
Base Fog	0.27	0.00	0.66	0.00	0.53	0.00	0.52	0.00

*15-min exposure.

†30-min exposure.

(a) UV FILTERED BROADBAND LAMP EXCITED FLUORESCENT IMAGE,
4-minute exposure at f4.7.
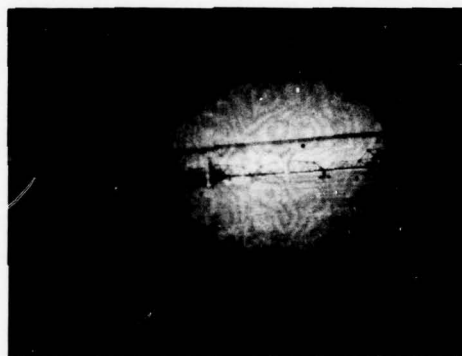
(b) ARGON LASER EXCITED FLUORESCENT IMAGE USING OPTICAL
CONFIGURATION I (see Figure 2), 45-second exposure at f4.7.
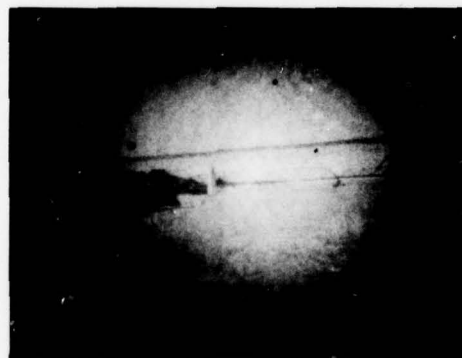
(c) ARGON LASER EXCITED FLUORESCENT IMAGE USING OPTICAL
CONFIGURATION II (see Figure 2), 3-minute exposure at f4.7.

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FIGURE 3   COMPARISON OF FLUORESCING RHODAMINE B POLAROID TYPE 55
PHOTOGRAPHS USING ARGON LASER CONFIGURATIONS AND
BROADBAND UV LIGHT SOURCE EXCITATION

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Image Processor Demonstration

The fluorescing images were also photographed using a Quantex low-light-level vidicon camera attached to a digital image memory/processor. During a manufacturer's demonstration, this system integrated the output of the fluorescing image in a manner analogous to photographic film, except that the image was digitized and stored in a computer. Once stored, the image could be viewed on a television monitor and evaluated. The processor allows variations in exposure time (intensification factor) and can internally change image contrast. Although this approach is not cost-effective as a research tool at this time, it should certainly be considered if the fluorescing image intensification technique is developed into an operational image intensification procedure for the Department of Defense or for commercial use.

V DELAYED FLUORESCENCE

The prime requirement for success of the fluorescing (or the chemiluminescing) image technique of photographic image enhancement is the achievement of a high signal-to-noise ratio. Unfortunately, many chemicals used in the manufacture of photographic films fluoresce when exposed to uv light. The plastic backing materials and almost all the gelatin substrates currently used in the industry fluoresce to some degree.

The deterimental effect of this undesirable accompaning fluorescence noise, that is, lower signal-to-noise ratio, is most severe if the fluorescing image is on the original negative film. This effect can be significantly decreased by the use of the dye image transfer technique, which allows the use of fluorescence-free materials.

It should, however, be possible to obtain the highest signal-to-noise ratio, and therefore the most successful image enhancement conitions, by using a combination of narrow-bandpass filters and dyes having a long fluorescence time constant relative to the background fluorescence (i.e., dyes exhibiting phosphorescence). By coordinating the excitation uv light and the delayed exposure of the fluorescing image, it should be possible to obtain the optimum signal-to-noise ratio.
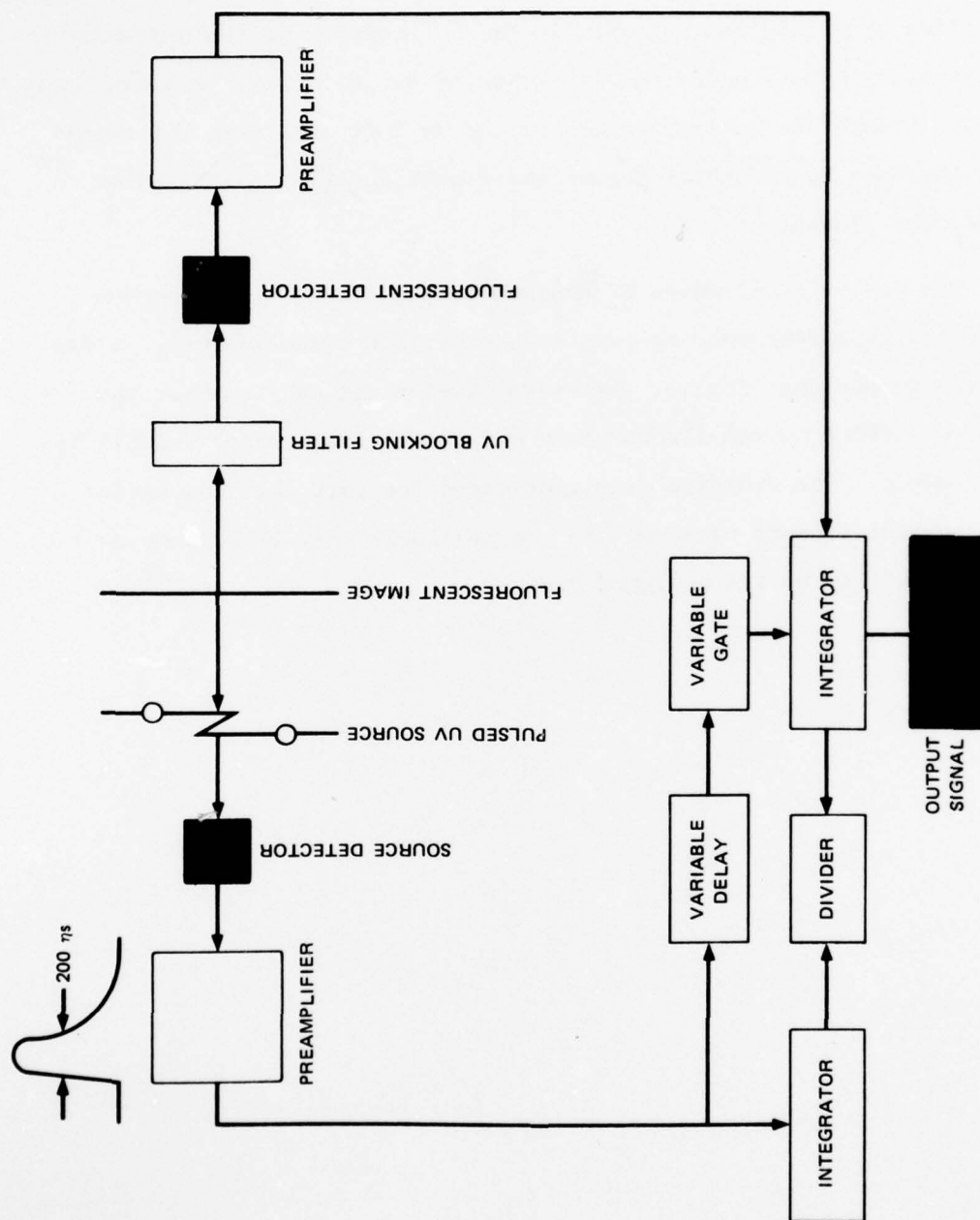
The Delayed-Fluorescence Detection Apparatus

A delayed-fluorescence detection apparatus was designed and partially constructed to evaluate the phosphorescence character of a number of different dyes. During our studies it became evident that the fluorescent activity of a dye is dependent on its chemical environment. Thus,

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we planned to evaluate the fluorescence lifetimes of promising dyes attached either to the original film or to the transfer film.

Figure 4 shows a block schematic diagram of the uncompleted delayed-fluorescence detection apparatus. Sparks were to be generated across a gap ($\approx$ 0.005 in.) between the ends of two electropolished 0.032-in. tantalum wires at a rate of approximately 5 kHz. The electrodes are housed in a fused quartz (Spectrosil) tube 1 mm i.d. and 2 mm o.d. for uv transmission. The signal from the source detector (HP 5082-4220) is amplified to produce a pulse $\approx$ 1 volt high and $\approx$ 200 ns wide at half height. A designed pulse-sensing circuit initiates a variable delay pulse, at the end of which a variable-width gating pulse is generated. The gate pulse is used to control the period during which the fluorescent radiation signal is measured. The fluorescent detector (HP 5082-4220) was designed to view the negative signal through a uv cutoff filter.

The design called for both pulses (source and fluorescent) to be fed to gated integrate and hold circuits. A bleed resistor is used across the holding capacitor, however, so that the results of integrating the pulses are held for a time much longer than the 200-ns pulse width but short enough for the integrated pulse to decay before the onset of the next pulse. The purpose of this approach is to stretch the pulses so that their duty cycle is sufficient to produce a dc signal by the use of a low-pass filter.

The designed output signal, which is proportional to Log (fluorescent light emission/uv incident light), would provide a calibrated determination of the timing circuit required for optimum signal-to-noise as well as a means of screening potential dyes for suitability and signal-to-noise characteristics.

FIGURE 4   DELAYED-FLUORESCENCE DETECTION APPARATUS

MA-5824-3

Reason For Incompletion of Apparatus

The design, construction, and testing of the delayed-fluorescence detection apparatus was assigned to Mr. M. Scolnick of the SRI Mass Spectrometry Center under the direction of Dr. M. Anbar. Approximately midway through the contract year, Dr. Anbar left SRI, with the result that the Mass Spectrometry Center was closed and Mr. Scolnick took employment elsewhere.

The cost-effectiveness of continuing the delayed-fluorescence detection apparatus was assessed and, under the circumstances, it was decided to postpone further apparatus development and increase the research effort on the fluorescence and chemiluminescence feasibility experiments. The decision also considered the fact that commercial delayed-fluorescence equipment is now available that would provide the same capability as the designed device.

VI   CHEMILUMINESCENCE

A review of the properties of compounds that have extremely intense chemiluminescent emissions has indicated that many are incompatible with photographic imagery. Some require the use of a nonpolar organic solvent, which will not diffuse into the original negative's gelatin to interact catalytically with image silver. Others are catalyzed by -OH groups and will therefore be activated by the photographic gelatin.

Luminol (5-amino-2,3,-dihydro-1,4-phthalazine-1,4-dione) is water-soluble and has a chemiluminescent behavior compatible with photographic film. The hydrogen peroxide oxidation of luminol in basic aqueous solution results in the emission of blue light[5] and is catalyzed by metal ions such as Cu(II), Ni(II), Cr(III), Mn(II), and Fe(II).[6,7] In principle, a photographic image toned with any of these ions should produce a chemiluminescent emission in an oxidizing solution. Copper (II) has been shown to be one of the most efficient catalysts for producing chemiluminescence and has therefore been selected for evaluation.

The research conducted to date includes chemiluminescence produced by photographic images toned with copper-ferrocyanide, copper-sulfide, and metallic-copper in an alkaline luminol-hydrogen peroxide solution. Methods used and data obtained in the preparation of copper-toned images are described below, together with data obtained from the investigation of the optimum luminol solution parameters.

Methods of Preparing Copper-Toned Images

Fully exposed resolution target images were used throughout this work except where noted. We first attempted to obtain copper ferro-cyanide images by toning the original negative images in a solution containing 0.35% cupric sulfate ($CuSO_4 \cdot 5H_2O$), 0.30% potassium ferricyanide ($K_3Fe(CN)_6$, and 2.8% sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) for 30 min. In this solution, which must be used within hours after mixing, images were gradually toned to a brown color indicating the formation of cupric ferrocyanide on the silver images. The images were then washed and the gelatin was hardened for 1 hr in a solution containing 10% formalin ($\sim$ 37% aqueous formaldehyde solution) and 2% potassium carbonate (K_2CO_3).

Copper sulfide-toned images were prepared first by forming the copper ferrocyanide-toned images in a solution of $CuSO_4/K_3Fe(CN)_6$ as previously described. After the images were washed with water to re-move the toning solution, they were prepared by a second toning in a solution of 2.5% sodium sulfide (Na_2S) for 10 min. The conversion of the brown copper ferrocyanide image to black copper sulfide was accom-panied by an increase in the optical density of the toned images. The film gelatin was rinsed thoroughly with water to remove sulfide solution and then hardened in a solution containing 10% formalin and 2% potassium carbonate.

Molenaar and co-workers[8] reported that it is possible to deposit copper metal on latent silver images using physical developers. This deposition of metal, which is an autocatalytic process, consists of an oxidation reaction followed by a reduction reaction. In the oxidation reaction the reducing agent Red in the developer gives up an electron to the nucleus of silver:

$$Red \longrightarrow Ox + e^- \qquad (1)$$
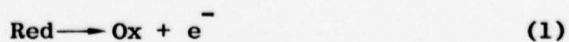
where Ox is the oxidized form of the reducing agent Red. (If the reaction is reversible, it is referred to as an redox system; an example is Fe^{3+}/Fe^{2+}). In the reduction a metal ion, in this case a copper ion, is reduced by the electron:

$$Cu^{2+} + 2e^{-} \longrightarrow Cu(s) \qquad (2)$$
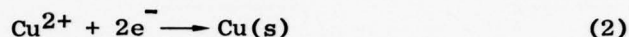
Both reactions take place at the surface of the photographic silver grain, so that the metallic silver acts as a nucleus and grows in size by the addition of copper atoms.

We first attempted to deposit metallic copper specifically on the silver images using a few of the physical developers as previously described. Our effort was unsuccessful, perhaps because these developers were unstable due to the simultaneous presence of the reducing agent and the metal ions. Physical developers have been formulated during our research that give superior results. These developers, which used a ferrous-ferric redox couple, contained different carboxylic acids such as tartaric acid, citric acid, and gluconic acid. We found that copper could be deposited effectively, on silver images by using sodium gluconate as the complexing agent for copper in the physical developer.

To prepare metallic copper-toned negatives, we used a physical developer comprising a copper complex in a ferrous-ferric redox system. The original negative images were washed in a 10^{-3}M potassium cyanide (KCN) solution for 30 min to reduce the base fog of the film. This step was necessary to prevent a significant amount of metallic copper from forming on the nonimage area of the film. Several water rinses were used to remove the cyanide solution from the gelatin. Since the physical developer was very sensitive to air oxidation, we found it was best to keep the solutions for the physical developer separate and mix them when needed. The composition of our best physical developer, consisting of two component solutions, is shown in Table 3.

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Table 3

COMPOSITION OF PHYSICAL COPPER DEVELOPER

Solution*	Component	Amount
A	Sodium gluconate (0.5MO	54.6 g
	Copper sulfate (0.06M)	7.6 g
	Cetyldimethyl benzyl ammonium chloride	0.5 g
	Sodium sulfite (0.2M)	10.4 g
	Water	To 500 ml
B	Sodium gluconate (0.5M)	54.6 g
	Ferrous ammonium sulfate (0.2M)	37.6 g
	Ferric nitrate (0.02M)	4.0 g
	Water	To 500 ml

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*The pH of the solutions was adjusted to 6.0 by adding 6M potassium hydroxide (KOH).

The physical developer was prepared when needed by mixing equal volumes of solution A and solution B. The original negative images were toned in the resulting solution at pH 6.0 by gentle agitation for 10 min. After toning, the film was rinsed a number of times to remove any physical developer from the gelatin. To maintain the integrity of the gelatin during chemiluminescent photography in alkaline luminol-H_2O_2 solution, it was necessary to harden the copper-toned film gelatin in a solution containing 10% formalin and 2% K_2CO_3 for 1 hr.

Preliminary studies on the deposition of metallic copper have been conducted using the physical development process with Eastman Kodak (EK) Film Types 5069, Plus-X and Tri-X. Currently, deposition of copper proceeds best on EK Type 5069 film. This was evident from the increase

in the optical density and the appearance of a bright reddish copper metallic luster on the images.

It has been shown that the metal spontaneously formed in the developer is negatively charged.[9] Therefore, these nuclei can be screened by a positively charged surfactant such as cetyldimethyl benzyl ammonium chloride. These positively charged groups appear to gather around the negative nucleus, while the apolar chains point out-ward from the nucleus. Thus, the enclosed nucleus will be surrounded by a second layer of surfactant caused by the apolar chain interactions, but this time the positively charged groups remain on the outside. This results in fairly large positively charged micelles; hence, metal ions in the developer cannot readily settle on the metal nuclei since they also carry positive charges. For the physical development of a silver image, the surfactant must not penetrate into the gelatin, because then the silver nuclei would also be screened.[10] Since the graininess of EK Type 5069 is considerably finer than either the Plus-X or Tri-X, we believe that the successful deposition of copper on only EK Type 5069 silver images is associated with the graininess of the film and the chain length of the surfactant used.

To obtain information on the amount of copper deposited relative to the original optical density of the image, we used physical developer to tone, for a fixed amount of time, strips of film containing properly exposed and underexposed images with various optical density of the images. This study enabled us to evaluate the relation between copper deposited and original optical density by measuring the optical densities of the images before and after toning with the physical developer. Figure 5 shows the results obtained from the toning of a strip of film, containing images with optical densities in the range between 0.10 and 1.24, in the physical developer for 10 min. The amount
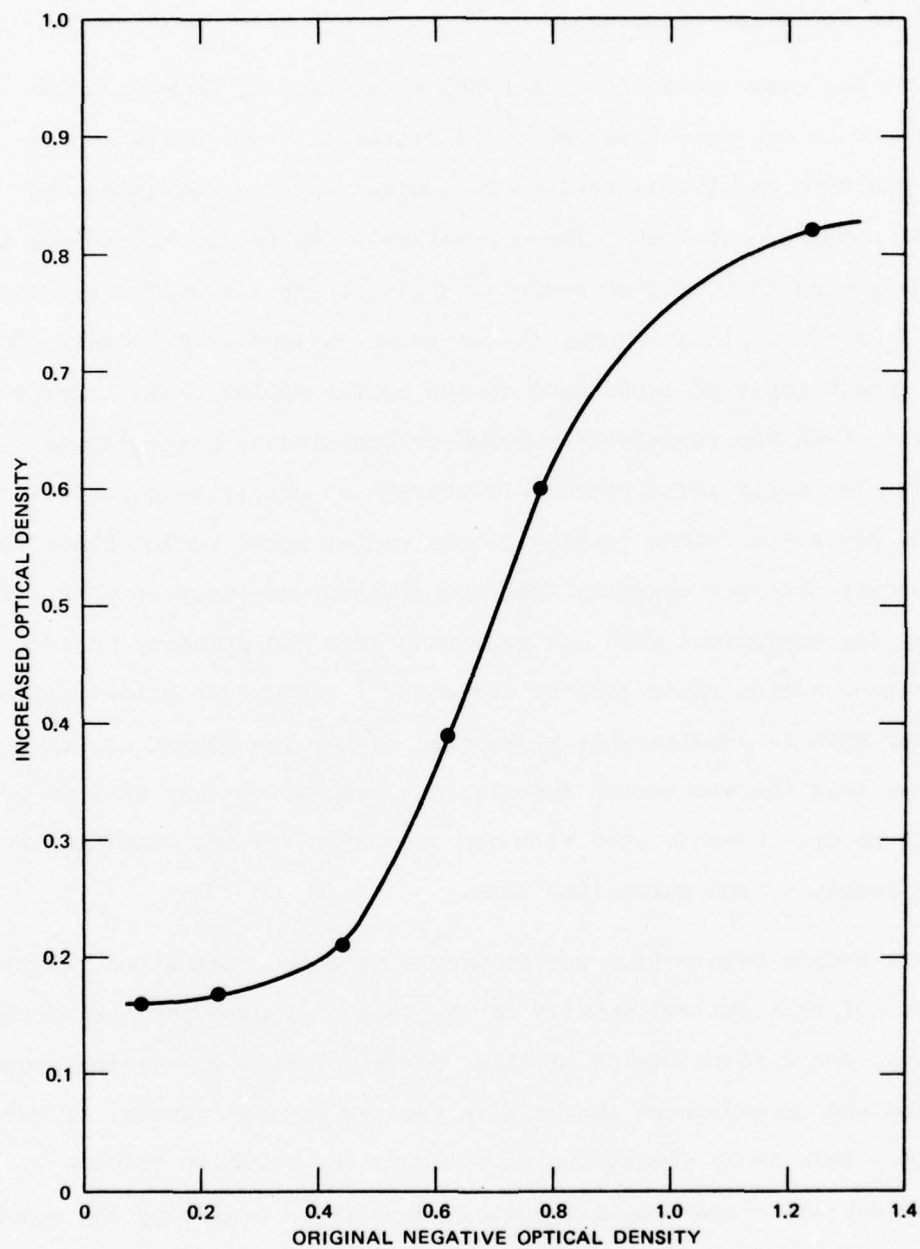
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FIGURE 5   THE AMOUNT OF METALLIC COPPER FORMED ON SILVER IMAGE AS
A FUNCTION OF ORIGINAL OPTICAL DENSITY

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of copper deposited on silver images is linear over a optical density range between 0.4 and 1.0. Furthermore, it appears that the amount of copper deposited can be controlled by careful selection of toning time.

Luminol Solution Parameters

Metal ions catalyze the oxidation of luminol by hydrogen peroxide in basic aqueous solution. This extensively studied reaction is one of the most efficient chemiluminescent reactions known. Thus, we chose to use luminol, which has a chemiluminescent behavior compatible with photographic film, as the preliminary luminescent agent for our studies. Of the metal ions that catalyze the oxidation of luminol, copper was used because of its high sensitivity in the alkaline luminol-H_2O_2 solution.[11] Moreover, the relative case with which copper complexes form specifically on silver images makes copper useful in chemiluminescent photography.

The chemiluminescence of luminol catalyzed by metal ions is extremely sensitive to solution parameters. Therefore, we studied various solution parameters, including types of oxidant, buffers, and chemiluminescent agent concentration. Results of these studies should allow us to define optimum conditions for the chemiluminescent photography of copper images. Luminescence measurements were made using a Turner Model-100 fluorometer without ultraviolet illumination. The relative luminescence intensity of the sample was measured by the photomultiplier of the instrument.

Types of Oxidant

Hydrogen peroxide (H_2O_2), sodium perborate ($NaBO_2 \cdot H_2O_2$) and potassium persulfate ($K_2S_2O_8$) were evaluated as potential luminol oxidants. Typically, 20 μl of 1.04 mM copper sulfate ($CuSO_4 \cdot 5H_2O$) was added to 4 ml of 5.6 mM luminol/2% K_2CO_3 solution (pH 11.6) in a round borosilicate

glass cuvette. Then small increments of 3% oxidant solution were added, and the luminescence was measured after each addition. The effect of hydrogen peroxide on the copper-catalyzed oxidation of luminol is shown in Figure 6. Each relative luminescence intensity data point shown is the average of two observations. The data show how variations in the hydrogen peroxide concentration affect the luminosity of the solution. These results indicate that the luminescence of Cu(II)-luminol solution oxidized by H_2O_2 remains at a maximum when the concentration reaches beyond 3 mM in a 5.6 mM luminol solution.

This finding is consistent with results obtained without copper ions[12] and suggests that it is possible to develop, in the Cu(II)-luminol solution, an optimum H_2O_2 concentration range that gives maximum chemiluminescent light emission.

The study of the effect of sodium perborate on the chemiluminescence of luminol was carried out by adding small increments of a 0.06 M $NaBO_2 \cdot H_2O_2$ solution (pH 12) to 4 ml of a 5.6 mM luminol solution (same pH) that also contained 20 μl of 1.04 mM Cu^{2+}. The luminescence was measured after each addition of oxidant. The effect of sodium perborate on the chemiluminescence of luminol is illustrated in Figure 7. The relative luminescence intensity plotted is an average of two observations. The data show that there is a decrease in the luminosity of the copper (II)-luminol solution with an increase in sodium perborate concentration. The maximum emission of chemiluminescent light occurs with 1-2 mM of $NaBO_2 \cdot H_2O_2$. This gradual decrease of luminescence with increasing concentration of sodium perborate may be due to the rate of decomposition of the perborate. The rate of decomposition has been found to increase with decreasing initial concentration of perborate in the presence of $CuSO_4$.[13] Thus, at high concentrations of perborate, a quenching effect would result due to the decomposition of the unstable copper peroxide formed in the solution. These experiments show that it is possible to obtain reaction conditions in which the emission of light can be maximized.

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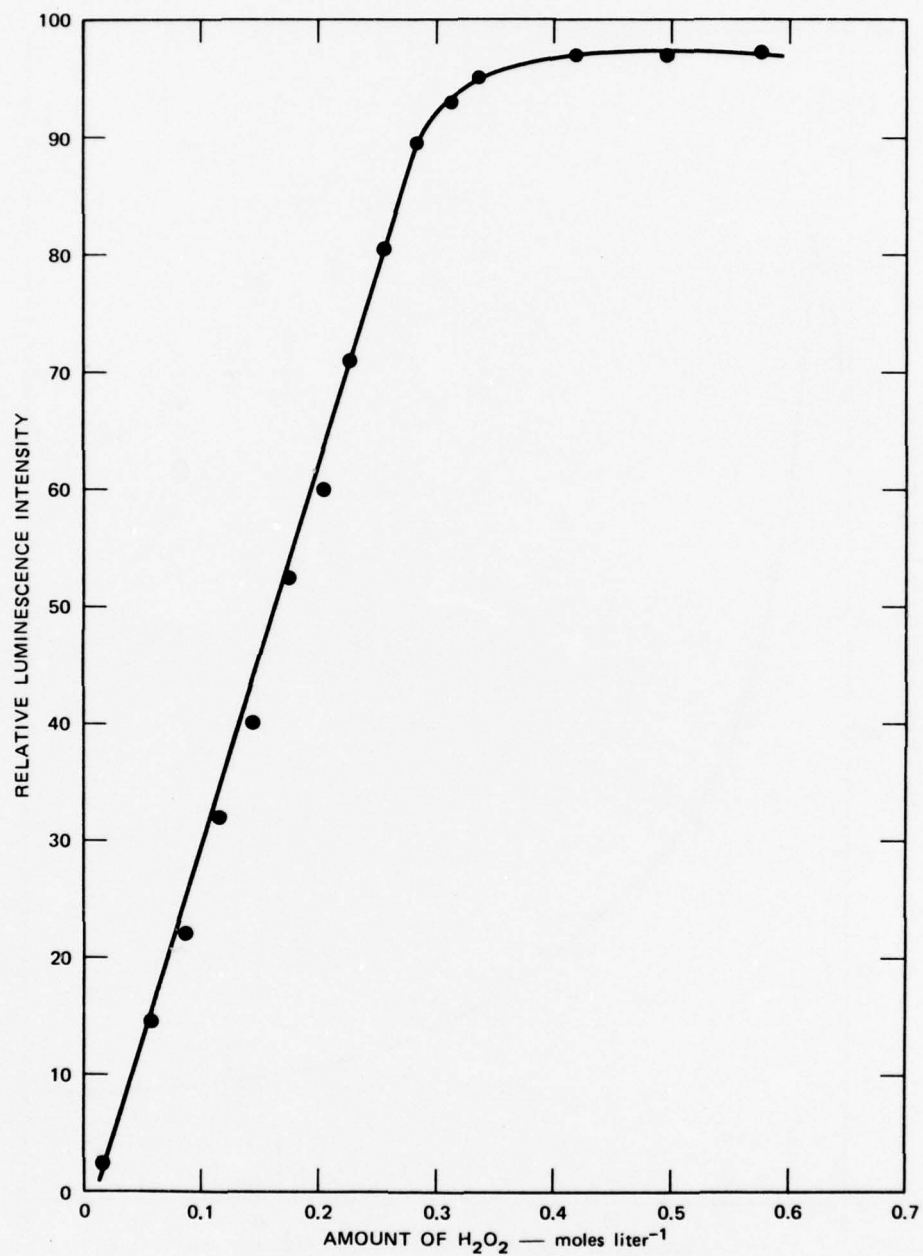
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FIGURE 6   THE EFFECT OF HYDROGEN PEROXIDE CONCENTRATION ON THE
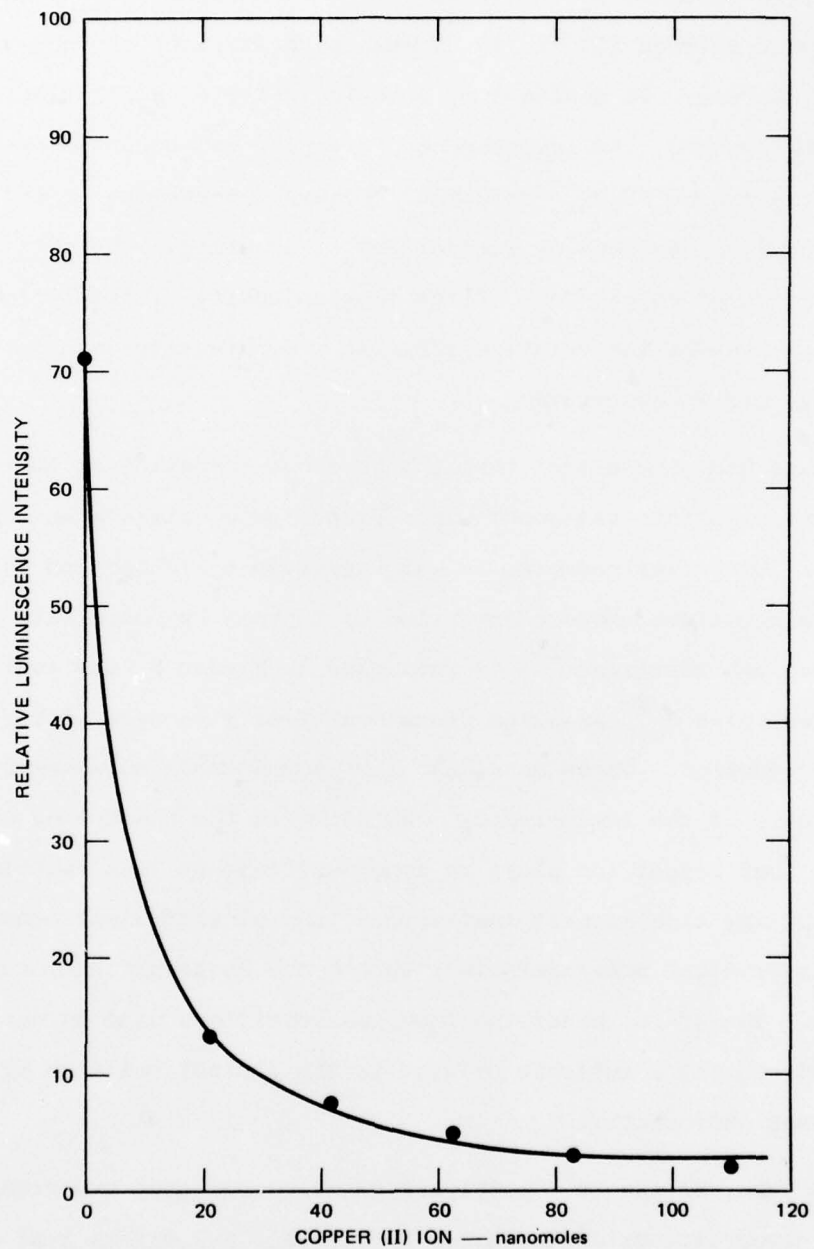CHEMILUMINESCENCE OF Cu(II)-LUMINOL SOLUTION
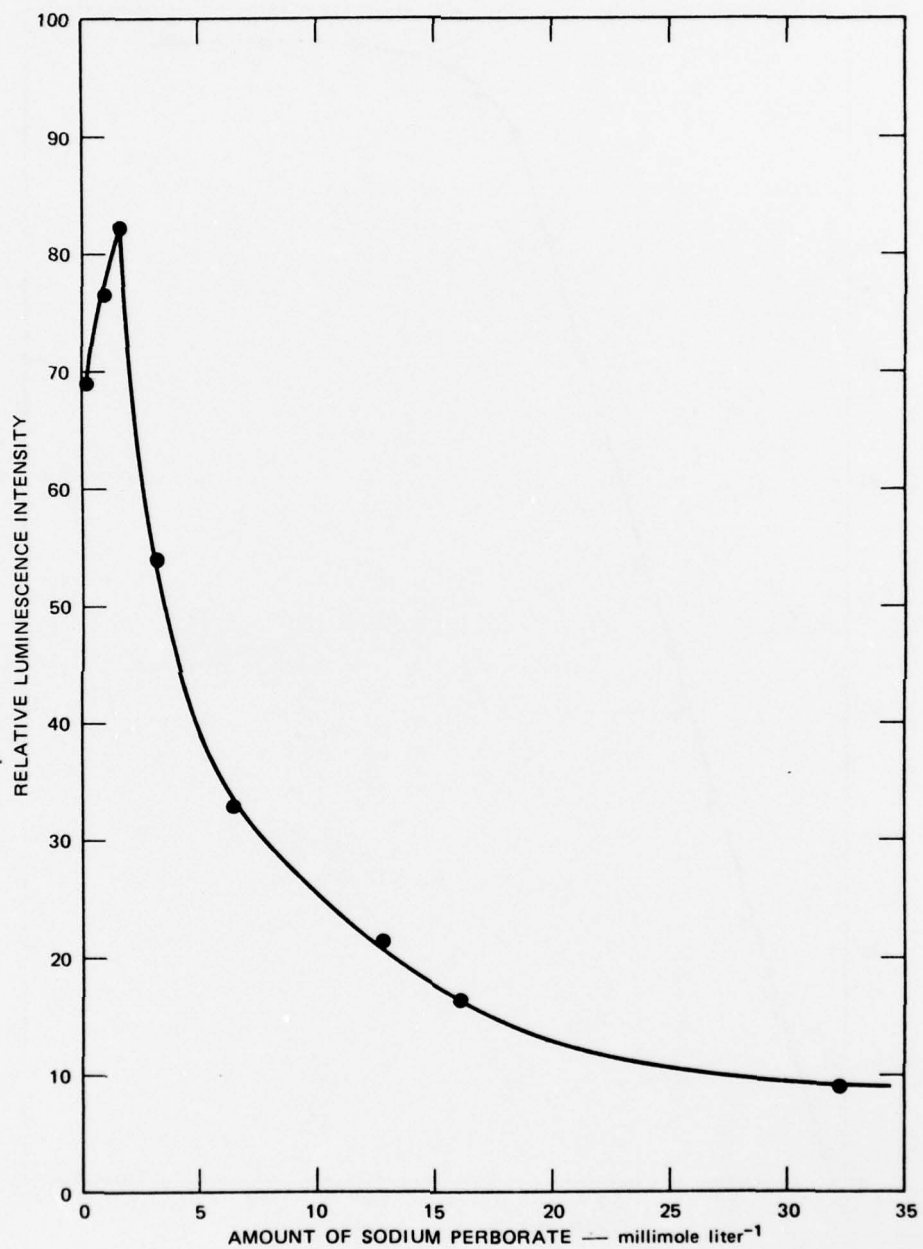
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FIGURE 7 THE EFFECT OF SODIUM PERBORATE CONCENTRATION ON THE
CHEMILUMINESCENCE OF CU(II)-LUMINOL SOLUTION

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As observed in other luminol-persulfate systems[14], the luminescence intensity is directly proportional to the concentration of persulfate in the range between 10^{-2} to 10^{-3} M when a small trace of copper ion is present. However, in contrast to both luminol-H_2O_2 and luminol-$NaBO_2 \cdot H_2O_2$ systems, the luminescence intensity was quenched by copper ions in the luminol-$S_2O_8^{2-}$ solution. Figure 8 shows the effect of Cu^{2+} on the chemiluminescence of luminol-$S_2O_8^{2-}$ solution. The data show how variation of copper ions affect the luminosity of the luminol-$S_2O_8^{2-}$ solution. Each of the relative luminescence intensity data points is an average of two observations.

It has been shown that chemiluminescence oxidation of luminol by potassium persulfate can occur under proper pH conditions in the absence of copper ions. Furthermore, it was suggested by Totter and co-workers that this chemiluminescence oxidation of luminol by persulfate may be due to radical reactions.[15] As indicated in Figure 8, the luminosity of the luminol-$S_2O_8^{2-}$ solution drops drastically to zero at higher Cu^{2+} ion concentration. These data, and the considerable enhancement of luminescence of the luminol-$S_2O_8^{2-}$ solution in the absence of Cu^{2+}, indicate that copper ion plays an important role in this reaction. These findings also suggest that copper ions at sufficient concentration may act as radical scavengers that quench the chemiluminescence of this reaction. Therefore, under the reaction conditions used in our tests, persulfate is not a suitable oxidant in the luminol solution of chemiluminescent photography.

The decay of the Cu^{2+}-catalyzed chemiluminescence was studied by adding appropriate oxidants (H_2O_2, $NaBO_2 \cdot H_2O_2$, $K_2S_2O_8$) to 4 ml of 5.6 mM luminol/2% K_2CO_3 solution containing 20 μl of 1.04 mM Cu^{2+} ions and measuring luminescence at various time intervals. The decay of chemiluminescence at 22°C using two different oxidants is depicted in Figure 9. Each data point is an average of two observations. As observed in

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FIGURE 8   THE QUENCHING EFFECT OF COPPER (II) IONS ON THE LUMINESCENCE
OF LUMINOL-$S_2O_8^{2-}$ SOLUTION

40
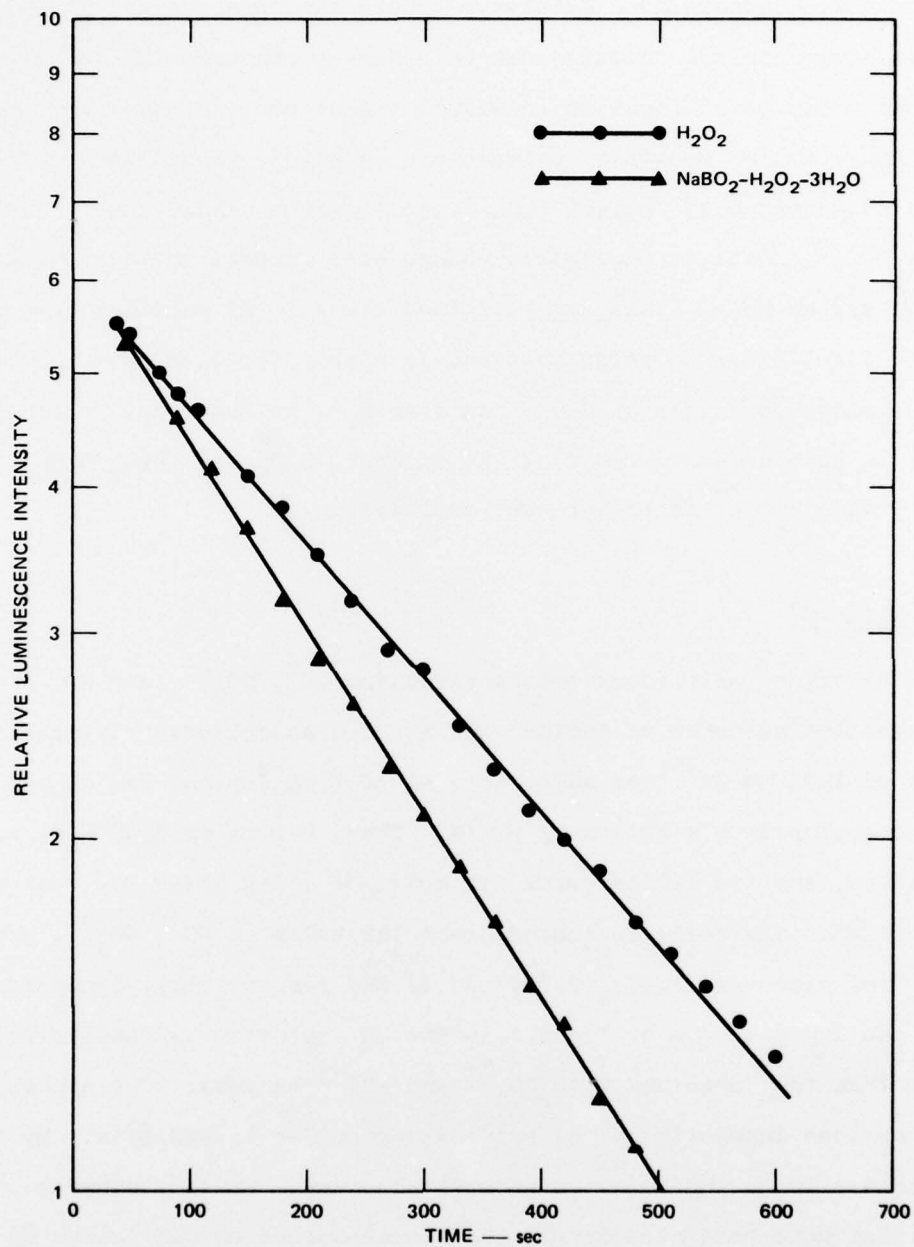
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FIGURE 9   THE CHEMILUMINESCENT DECAY OF COPPER (II)-LUMINOL SOLUTION
PRODUCED BY OXIDANTS H_2O_2 AND $NaBO_2$-H_2O_2-$3H_2O$

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another chemical system[16], the rate of chemiluminescence is first order in luminol, oxidants, and catalyst. These findings suggest that luminol concentration in the solution can in theory be manupilated to give optimal emission of light in chemiluminescent photography when combined with appropriate amounts of oxidant and catalyst. Furthermore, the chemiluminescence of luminol-$S_2O_8^{2-}$, unlike luminol-H_2O_2 and luminol-$NaBO_2 \cdot H_2O_2$, exhibited negligible change with respect to time during the first half an hour. This suggests that the rate of chemiluminescence is not first order in persulfate and is slow. The slow rate may be due to the slow hydrolysis of $S_2O_8^{2-}$ to give H_2O_2 in the reaction mixture. Thus, we have demonstrated that the oxidants H_2O_2 and $NaBO_2 \cdot H_2O_2$ are better than $S_2O_8^{2-}$ in the present application.

Buffers

The effect of various anions including OH^-, CO_2^{2-}, and BO_3^{3-} on the chemiluminescence of luminol was studied as follows: Typically, 20 μl of 1.04 mM Cu^{2+} was added to 4 ml of 1 mM luminol and dissolved in the appropriate solution at pH 12. Then, 0.1 ml of a 3% H_2O_2 solution was added, and the luminescence was measured 1 min after the reagents were mixed. The relative luminescence intensity in OH^-, CO_3^{2-}, and BO_3^{3-} solution were 1.5%, 29.5%, and 27.5%, respectively, indicating that the luminescence of luminol in the OH^- solution is considerably lower than that obtained with CO_3^{2-} and BO_3^{3-} buffers. The higher luminescence intensity in the buffers may be due to hydrolysis by the weak bases CO_3^{2-} and BO_3^{3-} in aqueous solution. Thus, the hydroxide ions that have been used in the chemiluminescence oxidation can be replenished by hydrolysis of the CO_3^{2-} and BO_3^{3-} ions.

Complexing Agents

The complexing agents ethylenedinitrilotetraacetic acid (EDTA), thiourea (H_2NCSNH_2), 2-mercaptoethanol ($HSCH_2CH_2OH$), potassium cyanide (KCN), and sodium citrate ($Na_2C_6H_5O_7 \cdot 2H_2O$) were tested with the Cu^{2+}-catalyzed luminescent solutions. It was found that all complexing agents except thiourea quench the light emission of the luminol, indicating that free Cu^{2+} ion plays an important role in the chemiluminescence oxidation of luminol. These experiments demonstrate that complexing agents can be used to suppress background luminescence that is caused by undesirable metal contamination.

Chemiluminescence Photography

The catalytic effect of copper and other trace metal ions in the alkaline luminol-H_2O_2 solution is so sensitive that even a small trace is enough to produce appreciable luminescence in the luminol solution. We attempted to reduce the metal-catalyzed background luminescence of luminol solution by introducting a chelating agent, such as EDTA, that will strongly complex the Cu^{2+} into the luminol solution. Another procedure investigated was circulation of the luminol solution through a column containing Chelex-100 resin (Bio-Rad, Richmond, Calif.) to remove copper ions. We have found that the circulating system is superior because the presence of complexing agent in the luminol-H_2O_2 system tends to rapidly dissolve the copper sulfide and metallic copper-toned images.

Figure 10 shows the apparatus used in chemiluminescing image photography. It consists of a 300-ml glass plate tank (10 x 10 x 3 cm) holding the basic luminol solution, a sintered-glass funnel containing Chelex-100 resin, and a Randolf vari-pump, Model-250 (Randolf, Co., Houston, Texas) to recirculate the solution at a rate of 140 ml/min during the operation process. The copper-toned negative was mounted on a
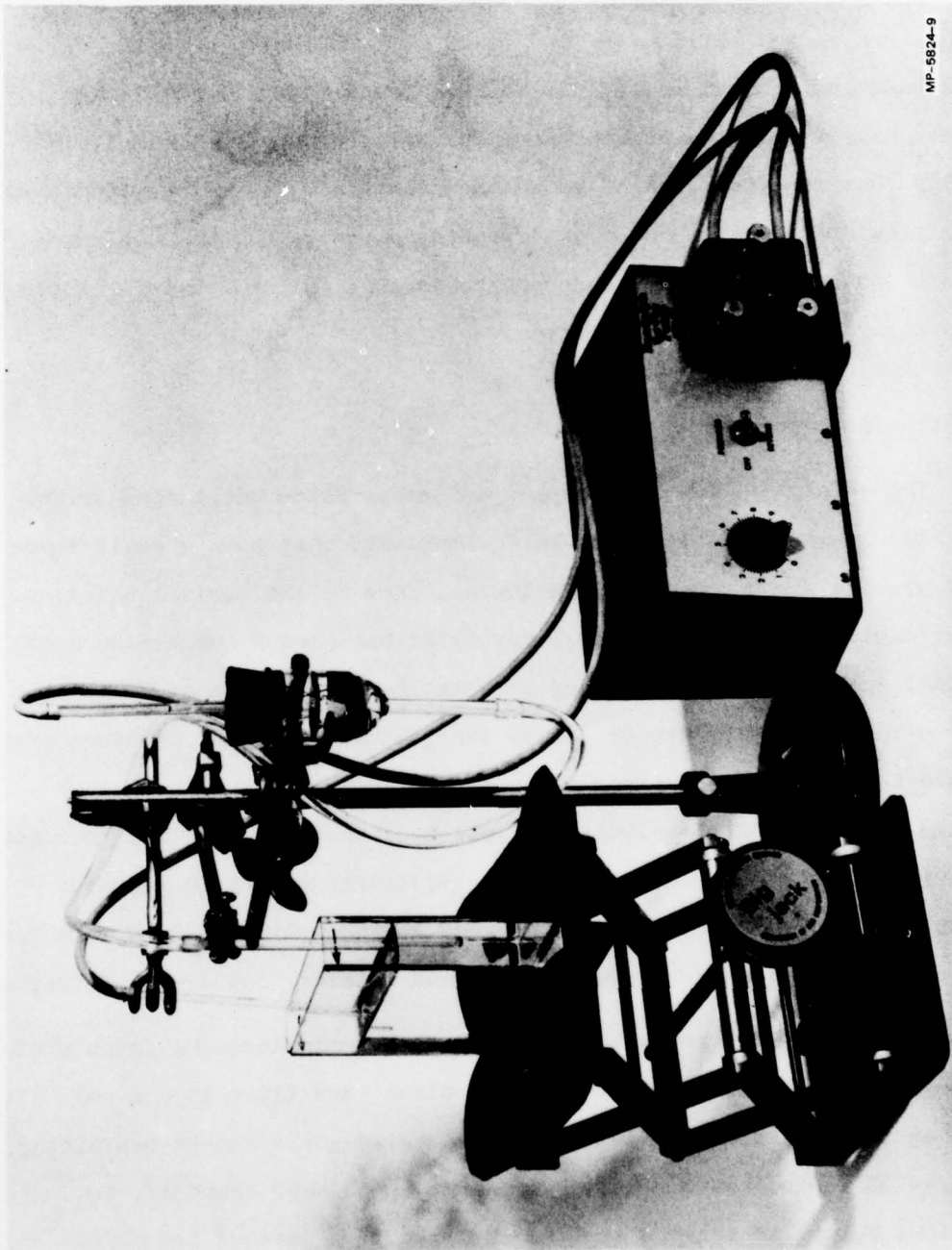
FIGURE 10   RECIRCULATING APPARATUS FOR CHEMILUMINESCING IMAGE PHOTOGRAPHY

MP-5824-9

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Lucite plate and submerged in the luminol solution. The chemiluminescing image was photographed using a Graflex Inc. Crown Graphic Model bellows camera equipped with a f 4.7, 135-mm Xenar lens. Polaroid Type 57 high speed 4 x 5 inches land film (3000 ASA) was used. Exposure times ranged from 10 to 30 minutes and were varied depending on the amount of copper deposited on the original negatives.

The best photographs obtained to date were made with a solution containing 5.6 mM luminol, 2% K_2CO_3, and 10^{-3} M H_2O_2. Large numbers of oxygen bubbles tended to form on the surface of the film when excess hydrogen peroxide was used. The combined effect of hydrogen peroxide and complexing agent caused the rapid deterioration of some toned images in the luminol solution.

The more soluble copper ferrocyanide-toned images were not useful under our test conditions. However, the more inert metallic copper- or copper sulfide-toned images were sufficiently stable in the alkaline-luminol-H_2O_2 solution. Figure 11 shows photographs taken in the flow system of the copper sulfide- and metallic copper-toned Itek resolution targets. The copper-catalyzed oxidation of luminol at the surface of a metallic copper- or copper sulfide-toned image gives intense chemiluminescence but resolution is low. The resolution of the image is degraded not only by the dissolution of the catalytic metallic ions but also by the inefficient removal of metallic ions from the solution in the vicinity of the image.

Conclusions

The results of experiments conducted in this research program show that it is possible to prepare copper sulfide- or metallic copper-toned images in a rapid and relatively easy way. The gelatin of the film hardened with 10% formalin/2% K_2CO_3 solution can withstand the alkaline

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(a) COPPER SULFIDE-TONED ITEK TARGET, EXPOSURE TIME 30 MINUTES
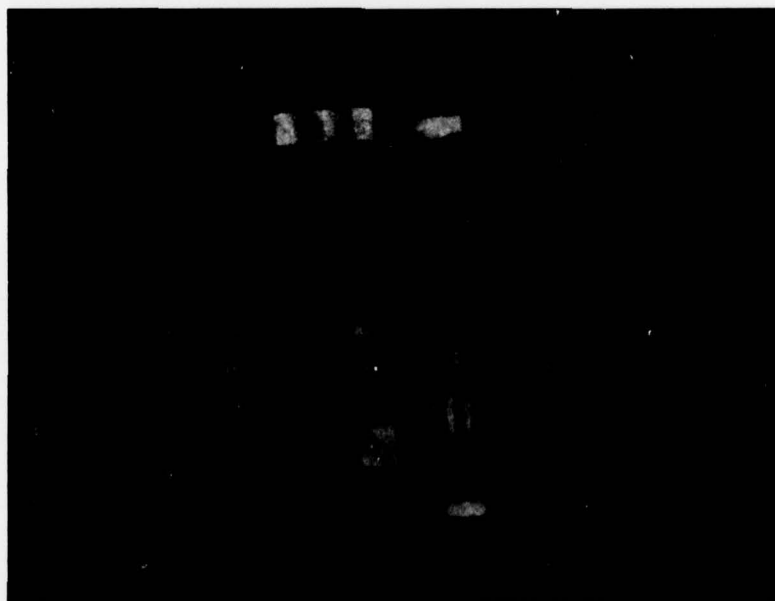
(b) METALLIC COPPER-TONED ITEK TARGET, EXPOSURE TIME 15 MINUTES

MP-5824-10

FIGURE 11   POLAROID TYPE 57 PHOTOGRAPHS OF CHEMILUMINESCING IMAGES

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luminol-H_2O_2 solutions used. Although the detailed mechanism of Cu^{2+}-catalyzed luminescence of luminol is not fully understood, we were able to develop useful procedures to rephotograph chemiluminescing images.

These experiments also demonstrate that chemiluminescence photography can be useful in photographic image enhancement. However, we are currently limited by the optical systems used and by the ineffectiveness of the present circulating system.

VII   SUGGESTIONS FOR CONTINUED RESEARCH

During the contracted year of research, we have demonstrated the feasibility of using chemiluminescence and fluorescence to intensify photographic imagery. The overall objective of continued efforts should be to improve both these promising approaches and to quantitatively evaluate their capabilities and limitations. Specific recommendations for each technique are described below.

Additional fluorescent dyes should be evaluated for high signal-to-noise ratios and uv-illuminated lifetimes. Further research and development is necessary to improve the fluorescent dye technique that transfers the image to a nonfluorescing support. Support materials should be evaluated for image transfer efficiency and undesirable fluorescence characteristics.

To improve the signal-to-noise ratio of the fluorescence technique, it is necessary to evaluate the low-level emission fluorescence spectra of all materials used. In addition, the optimum uv excitation wavelength for each dye under investigation must be determine by the use of a high resolution spectrofluorometer.

The copper-catalyzed oxidation of luminol at the surface of a metallic- copper- or copper-sulfide-toned image gives intense chemiluminescence, but of low resolution. The resolution is degraded because the catalysis takes place only with the catalytic metallic ions as they dissolve from the image and enter the solution. Unfortunately, the ions are then free to migrate and catalyze chemiluminescence away from their original image sites. This problem has been partially solved by the addition of a crude ion exchange, slow turnover recirculating system.

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It is suggested that a large-volume, rapid-flow recirculating system be constructed. Such an apparatus should greatly increase the resolution of the resulting imagery by reducing the effective mean lifetime (and therefore range) of migrating ions and chemiluminescing molecules.

Solution characteristics must be further improved so that an image can be obtained that will chemiluminesce for a sufficient duration and intensity to give a series of intensified photographs before retoning is required. Solution characteristics that are sensitive and, therefore, require further investigation are oxidant type, oxidant concentration, chemiluminescent agent concentration, pH, temperature, and recirculating flow rate.

Manuscripts are currently in preparation for documentation of the above results in the scientific literature.[17,18] In addition, a patent disclosure describing the techniques of fluorescence and chemiluminescence photographic image enhancement will be filed with the U.S. Patent Office.[19]

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